Adaptive Process Controls and Ultrasonics for High Temperature PEM MEA Manufacture

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MN005

Overview

Timeline

- Project start date: 9/01/08
- Project end date: 9/30/12
- Percent complete: 85%

Barriers Addressed

- A. Lack of High-Volume Membrane Electrode Assembly (MEA) Production
- F. Low Levels of Quality Control and Inflexible Processes

Budget

- Total project funding: $2,508,186
  - DOE share: $1,611,129
  - Contractor share: $897,057
- Funding received in FY11: $305,895
- Funding for FY12: $250,000 (so far)

Partners

- RPI CATS- Project Lead
- ASU- Subcontractor
- BASF Fuel Cell- Collaborator
- PMD- Collaborator
- UltraCell- Collaborator
- NREL- Collaborator
- Ballard- Collaborator

Relevance

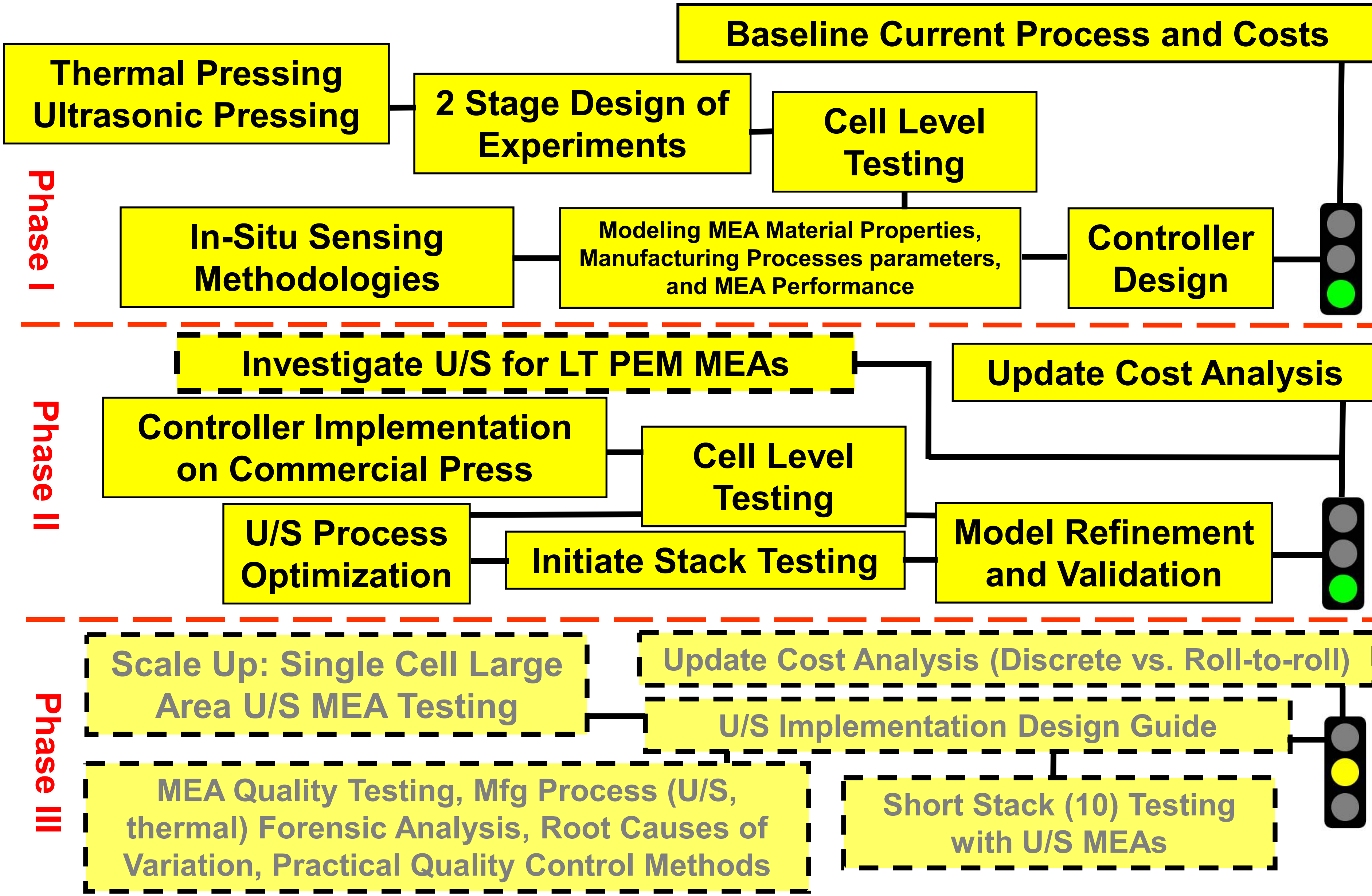
Situation and Objectives

- Situation: In spite of the fact that there are variations in MEA component material properties, industry uses the same manufacturing process parameters for each one fabricated. This results in variations in MEA properties and performance, and the potential for stack failures and re-work, and reduced durability.
- We need to develop a deeper understanding of the relationships among MEA material properties, manufacturing processes parameters, and MEA performance (3Ps).
- The high level objectives of the proposed work are to enable cost effective, high volume manufacture of high temperature (160-180°C) PEM MEAs by:

Specific Objective	Barrier Addressed
1. Significantly reducing MEA pressing cycle time through the development of novel, robust ultrasonic (U/S) bonding processes for high temperature (160-180°C) and low temperature (<100°C) PEM MEAs	A. Lack of High-Volume MEA Production
2. Achieving greater manufacturing uniformity and performance through (a) an investigation into the causes of excessive variation in ultrasonically and thermally bonded high temperature MEAs using more diagnostics applied during the entire fabrication and cell build process and (b) development of rapid, yet simple quality control measurement techniques for use by industry.	F. Low Levels of Quality Control and Inflexible Processes

Technical Approach

Project Plan



Phase I

Task	Description	Results/Conclusions	Completion
1.0	Baseline and Analysis of Current Process	Initial cost model developed	100%
2.0	Comparison of Current and Proposed MEA Pressing Processes	Hardware, tooling, and protocol for thermally and U/S bonding of MEAS achieved	100%
3.0	Baseline Process Testing	Performance of thermally and U/S bonded MEAs quantified and shown equivalent to commercial product	100%
4.0	Model Development	Combined dynamic/FEA model demonstrated	100%
5.0	Development of In-situ Sensing Techniques	Adaptive process control via in-situ AC impedance measurement demonstrated	100%
6.0	Controller Development	Control performed manually	100%
7.0	Phase I program review	Go Decision	100%

Blue shading indicates tasks performed during FY2011 and covered in Accomplishments & Progress section

Technical Approach

Phase II

Task	Description	Results/Conclusions	Completion
8.0	APC Implementation	Convergence of AC real impedance (1 kHz) to small value signifies complete bonding $\rightarrow$ 30 to 7 sec reduction in sealing time	100%
8.1	APC for Ultrasonics	Acoustic signal sensing inconclusive, but U/S process robustness and speed lessen need for APC anyway	100%
9.0	Evaluation of MEA Performance	Five-cell stack testing for 50 cm^2 cells demonstrated	100%
9.1	Evaluation of Larger Scale Ultrasonically Sealed MEAs	140 cm^2 cell and hardware designs successfully demonstrated and experimental testing is on-going.	100%
9.2	Ultrasonic Sealing Process Optimization	2 sec bonding time; post heat treatment is the dominant process parameter	100%
9.3	Heat Treatment Process Optimization	Heat treatment time can be reduced by 50% at higher temperature	100%
9.4	Evaluate Feasibility of Ultrasonic Sealing and APC for Low Temperature MEAs	For 10 cm^2 size using optimal conditions, U/S bonding showed 94% cycle time and 98% energy reduction compared to thermal bonding. O_2 performance same, but air slightly degraded.	100%
9.5	Durability Testing of Ultrasonically Sealed MEAs	Ultrasonically sealed MEAs with optimized process parameters exhibited no cell voltage degradation and minimal Δcell internal resistance during the 200 hour tests	100%
10.0	Updated Cost Analysis	Conservatively, cost reductions of 29% for APC, and 90% for U/S bonding	100%
11.0	Phase II program review	Go Decision	100%

Phase III

Task	Description	Status	Completion
12.0	Short Stack Testing	Ten-cell stack performance and endurance tests with thermally and U/S bonded MEAs are on-going	60%
13.0	Testing of High Temperature MEAs with Larger Active Area	Performance tests are on-going for thermally and U/S bonded MEAs	75%
14.0	Quality Testing of Thermally and Ultrasonically Bonded High Temperature MEAs	Analytical techniques used to characterize bonding effectiveness during pre-cell assembly and performance during post-cell assembly	50%
15.0	Expanded Cost Analysis	New cost, cycle time, and energy consumption data acquired	25%
16.0	Ultrasonic Bonding Implementation Design Guidelines	Will begin after completion of Tasks 12-14.	25%
17.0	Phase III Program Review	Expected in Fall 2012	0%

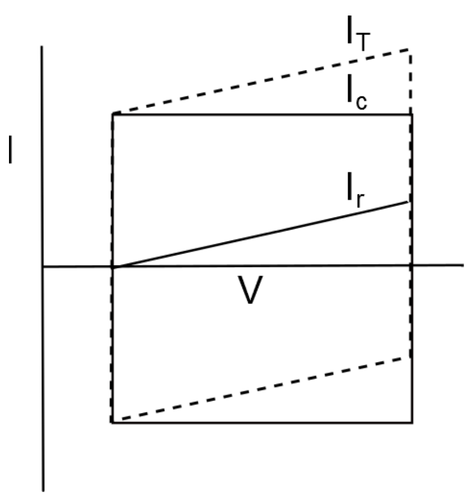
Approach to Accessing the Effect of MEA Bonding Method on Performance and Structure (Tasks 8.0 & 14.0)

- Vary the MEA bonding method on 50 cm^2 cells
  - Ultrasonic Bonding (1-2 seconds)
  - Thermal Bonding (30 seconds)
- Bonding effectiveness pre-cell assembly
  - Mechanical bond strength (Instron)
  - Catalyst-electrolyte contact area and cell shorting (Electrochemical Diagnostics)
  - Platinum crystallite size (XRD)
- Effect on performance post cell assembly
  - Cell performance (VI curves)
  - Isolation of losses (Electrochemical Diagnostics/ In progress)

MEA Quality Control Pre-Cell Build Using Cyclic Voltammetry

Cyclic Voltammetry:

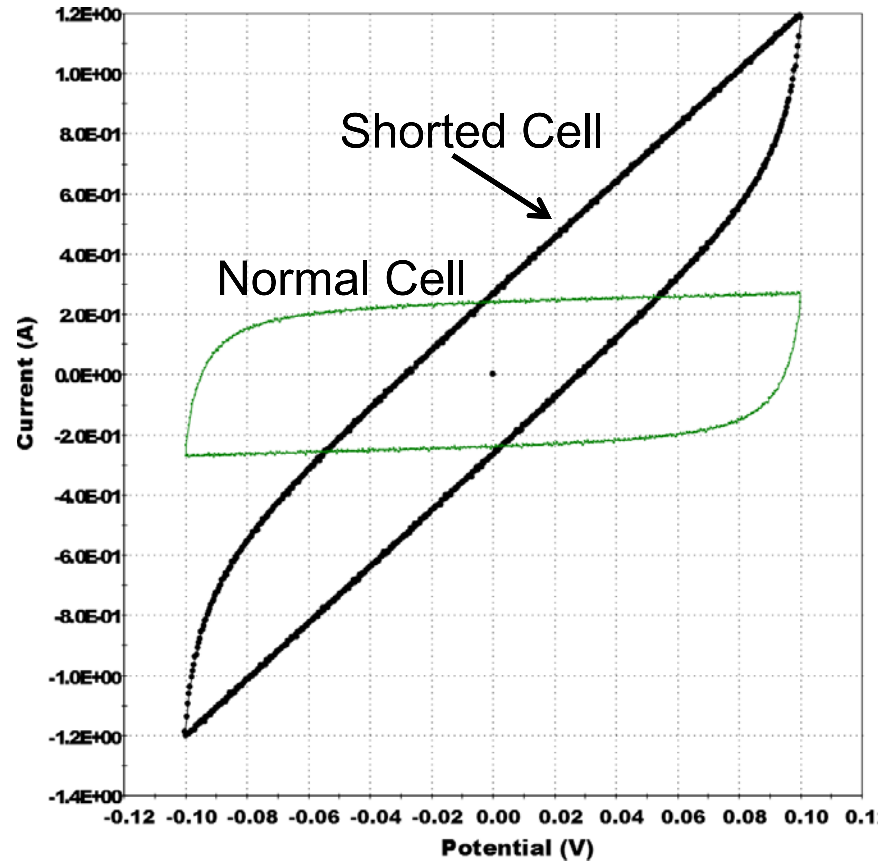
- High slope of the I/V relation indicates a shorted cells
- Low capacitive current indicates pore electrolyte/ electrode bonding
- Fast 0.5 - 4 second cycle time depending on scan rate



$$I_T = I_{cap} + I_{res}$$

$$I_c = \frac{dQ}{dt} = C_d A v$$

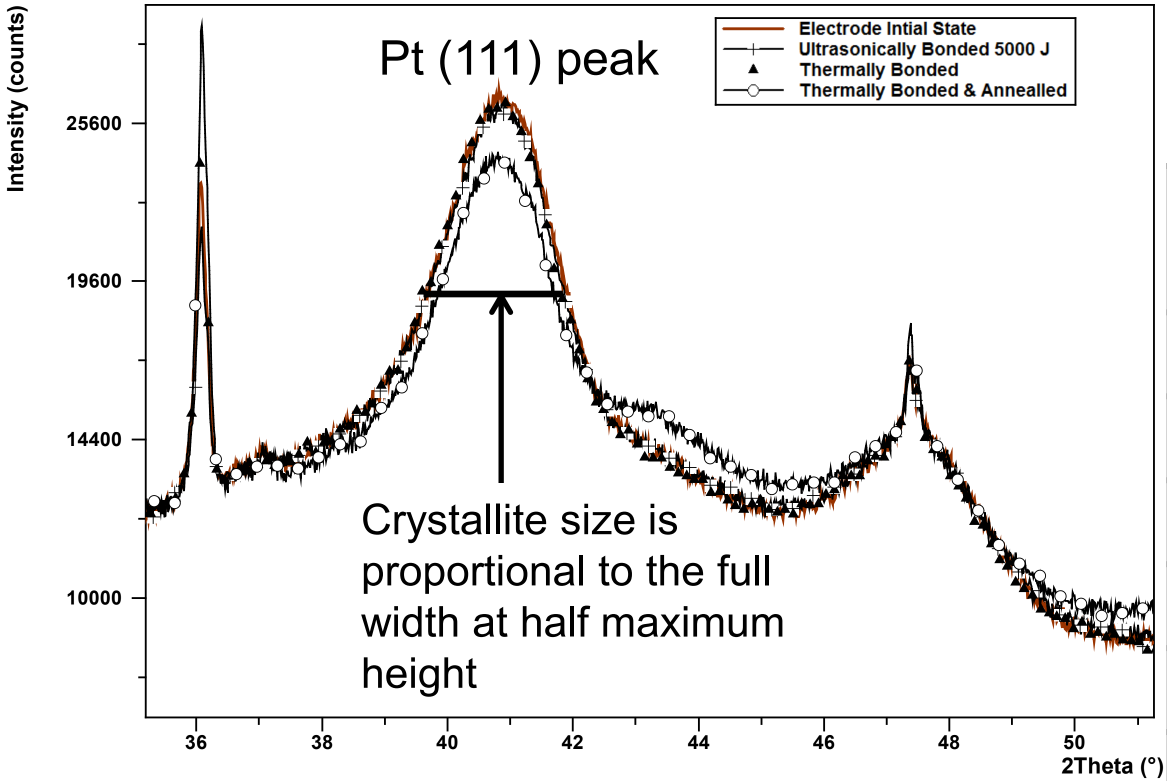
$$I_r = V/R_{e-}$$



	Slope (1/R)	
Fabrication Step	Normal Cell	Shorted Cell
U/S Bonded	0.034	0.109
Annealed	0.171	0.785
Post Cell Build	0.311	9.334

Accomplishments & Progress

XRD Before and After Bonding



$$t = \frac{.9\lambda}{B\cos\Theta_B}$$

T = crystallite size

λ = X-ray wavelength (Cu $K_{\alpha 1}$ & $K_{\alpha 2}$)

B = peak width in radians

Θ_B = peak angular position

	FWHM (degrees)	Crystallite Size (nm)
Initial Cathode (Run 1)	1.99	4.3
Initial Cathode (Run 2)	1.98	4.3
Initial Cathode (Run 3)	1.97	4.3
5000 J Ultrasonic (Run 1)	1.98	4.3
5000 J Ultrasonic (Run 2)	2.20	3.9
5000 J Ultrasonic (Run 3)	1.96	4.3
Hot Pressed	1.94	4.4
Hot Pressed and Annealed	1.86	4.6

Peak width does not increase with U/S bonding, i.e. no evidence that the catalyst crystallite size increases

Effect of MEA Bonding Method on Fuel Cell Performance

Results Summary for Ten 50 cm^2 Cells Fabricated with Each MEA Bonding Method

Bonding Method		1000 Hz Ohmic Impedance @ 1000 Hz (Ohms)	Tafel Slope (V/Decade)	Current @ 0.85 Volts with Oxygen (A/cm^2)	Cell Voltage at 0.2 A/cm^2 air on the cathode	Oxygen gain at 0.6A/cm^2 (Volts)
Thermal	Average	2.3	0.119	0.020	**0.637**	0.108
	Standard Dev.		0.008	0.004	**0.013**	0.007
Ultrasonic	Average	2.3	0.104	0.015	**0.650**	0.099
	Standard Dev.		0.007	0.003	**0.009**	0.009

1. Performance is slightly higher for MEAs bonded with the U/S method
2. Phase 2 testing is on going to determine the cause of variations in cell performance
3. Early Phase 2 cell voltages are 20-30 mV higher than the results above with reduced variation
4. CV and impedance diagnostic data is being obtained for both bonding methods

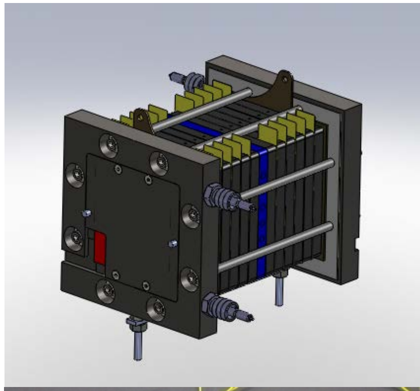
Test conditions for all tests:
160^0C Cell Temperature
1.2 H_2 stoich
2.5 Air/O_2 stoich

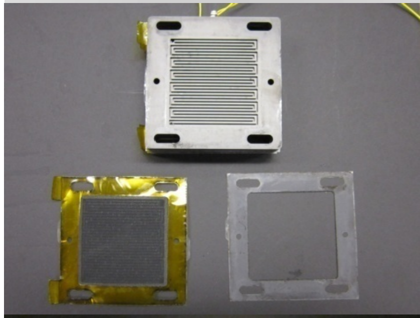
Thermal sealing parameters:
1. Temperature 140^0C
2. 25% compression

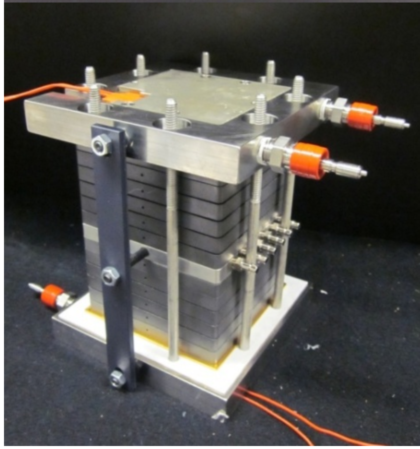
Ultrasonic sealing parameters:
1. 2000 J
2. 60 psi (0.44 N/mm^2)
3. 20 kHz frequency
4. 2.5X amplitude booster

Results of Short Stack Testing (Tasks 9.0 & 12.0)

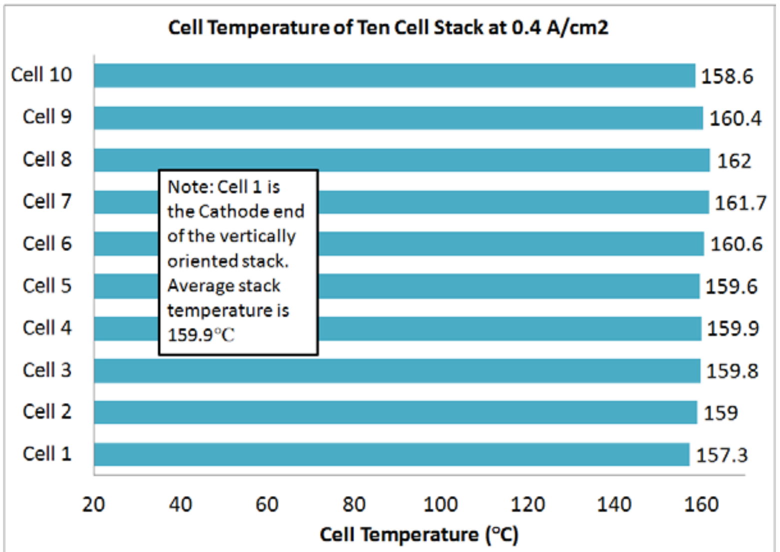
- A fuel cell stack was designed that can accommodate up to ten 50-cm^2 cells and three cooling plates
- Stack was designed with same flow field configuration as single cell hardware to correlate performance results
- 5- cell and then 10-cell insulated stacks are being tested to gain insight into cell performance in a stack as well as heat generation and distribution
- Stack burn-in is for 13 hours at 0.2 A/cm^2
- Polarization curves are taken for air and O_2 at end of burn-in with 1.2 H_2 and 2.0 Air/O_2 stoichiometric ratios
- Investigate manufacturing-attributable cell-to-cell variation under realistic conditions



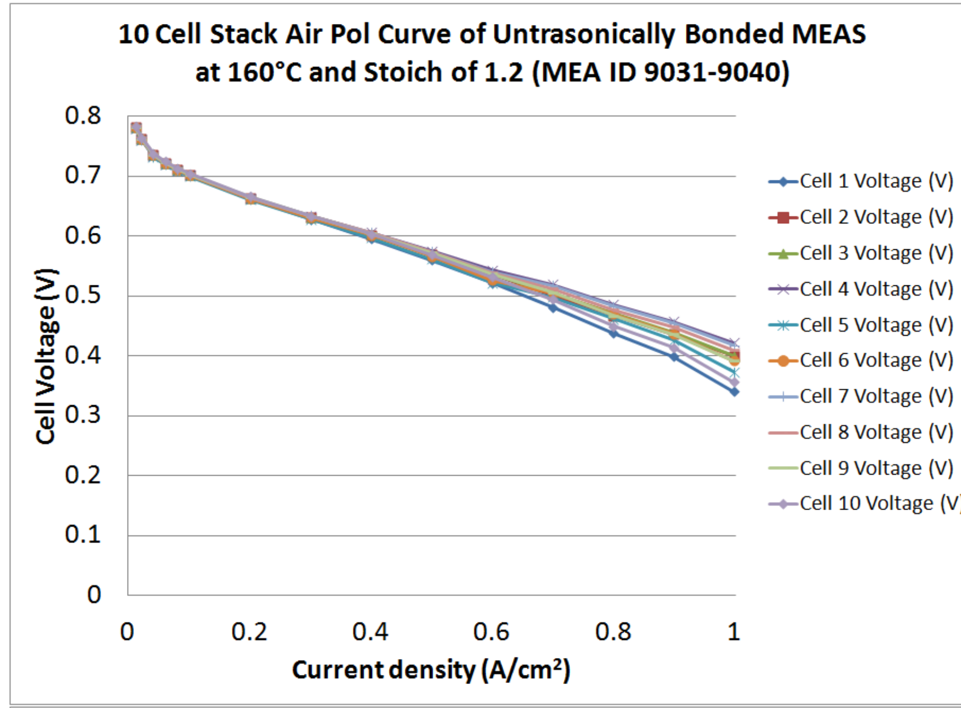


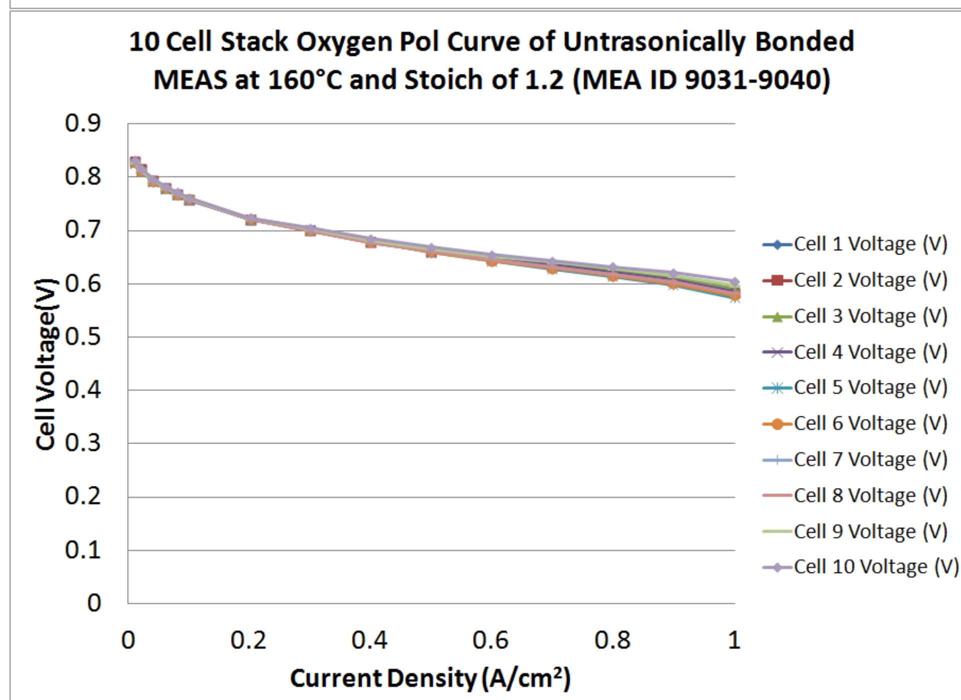


Accomplishments & Progress



Temperature profile (bottom to top) of 10-cell stack with air, ΔT = 162 – 157.3 = 4.7ÁC

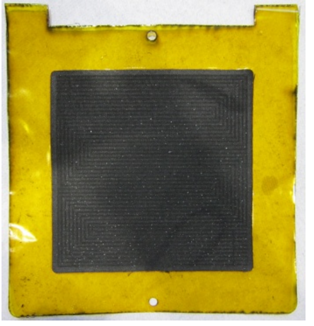


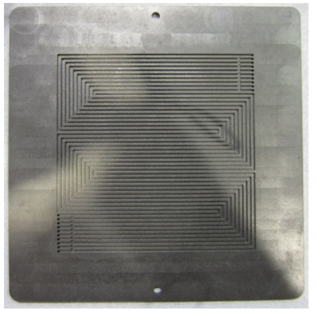


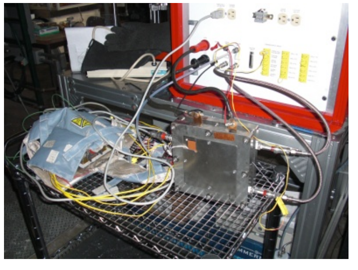
Accomplishments & Progress

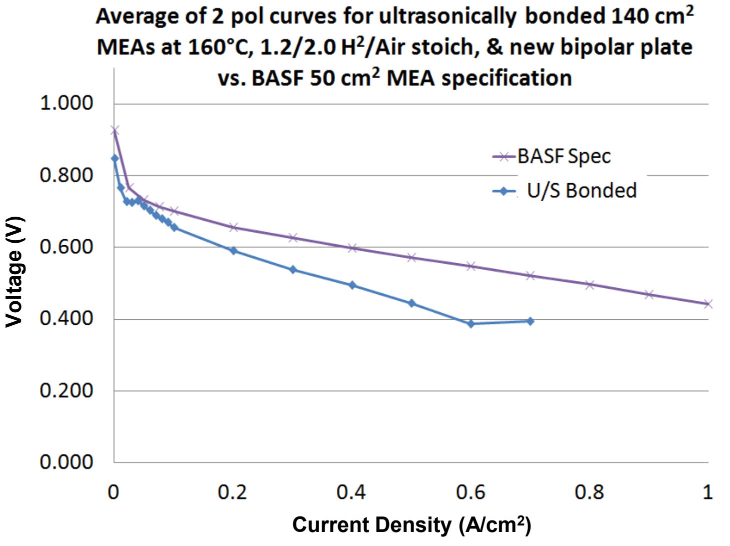
Testing of High Temperature MEAs with Larger Active Area – 140 cm^2 (Tasks 9.1 & 13.0)

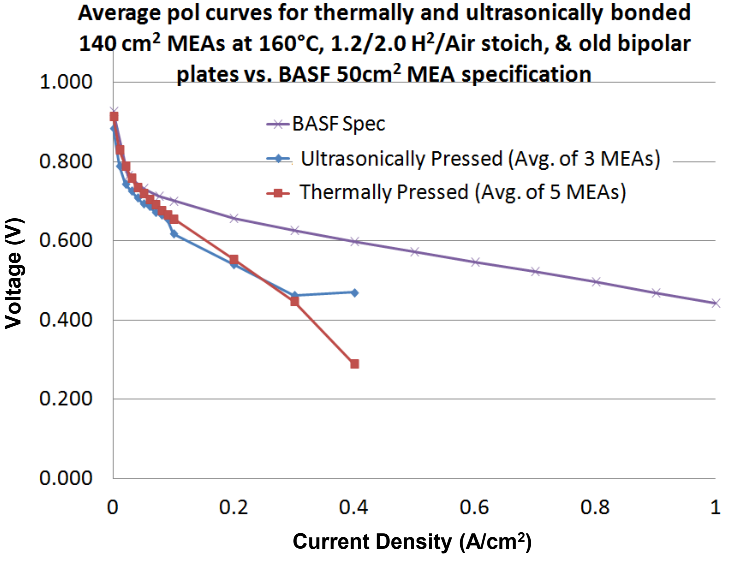
- Single cell testing hardware completed
  - Polarization curves for 140 cm^2 MEAs are compared to 50 cm^2 MEA BASF specification
- Bipolar Plates (BPP) Redesigned
  - Old graphite plates suboptimal
  - New machined composite plates with optimized flowfield
- U/S and thermally bonded 140 cm^2 MEA performance with old BPP is similar, although worse than BASF specification for 50 cm^2 MEAs. U/S MEAs show improved performance with new BPP. Investigation into systemic causes of deviations is on-going.





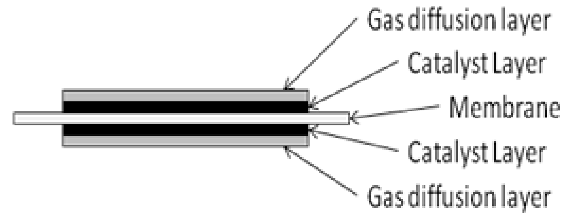


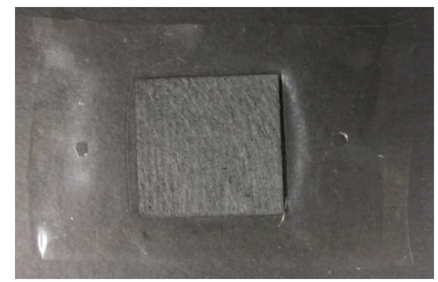


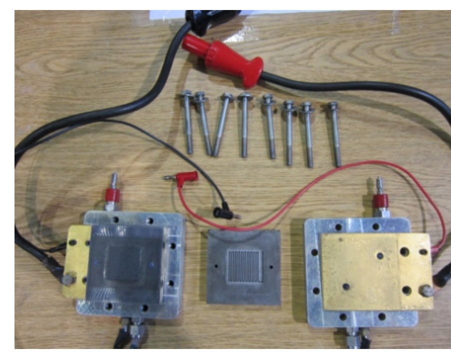


Ultrasonic Bonding of Low Temperature MEAs (Task 9.4)

- 10 cm^2 active area, Nafion® 115, commercial and custom-made GDEs designed for thermal pressing
- Custom fixtures, tooling, test hardware
- Design of Experiments, ANOVA
  - Optimization, Estimate main/interaction effects
- Performance characteristics
  - Pol. Curves, Impedance scans, cyclic voltammetry
- Comparison to thermally pressed optimization

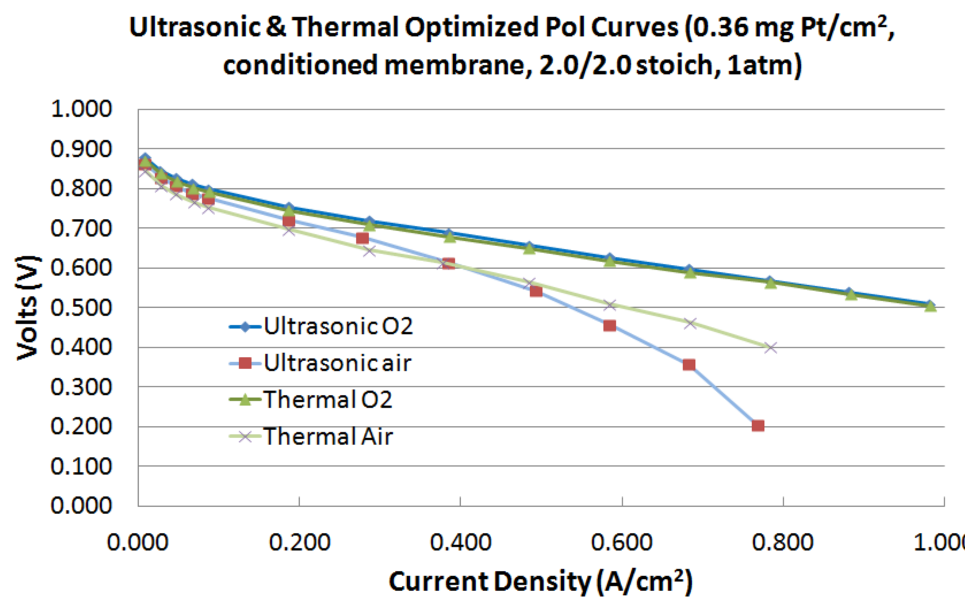






Results

- Effect of electrode architecture on ultrasonic bonding
  - Very sensitive
- Ultrasonic optimization
  - Energy flux: 9.0 J/mm^2 and Pressure: 3.0 N/mm^2
  - No main effect of Energy or Pressure, No interaction effect



- Thermal pressing optimization
  - Temp:170°C , Pressure: 2.0 N/mm^2, Hold time: 120 seconds
  - Main effect of temperature ($P<0.01$). No main effect of pressure.
- Manufacturing process & membrane condition study
  - U/S > Thermal by ~20 mV at all oxygen and low air A/cm^2
    - U/S exhibit high diffusion and mass transport losses
  - Conditioned membrane → ~40 mV increase

Manufacturing Cost Analysis (Tasks 10.0 & 15.0)

- Factors included: capital depreciation; tooling; labor; electricity; chilled water; HVAC; maintenance; space; waste disposal cost
- Component materials were not included in analysis
- Assumptions:
  - Baseline case is current BASF Fuel Cell process/system
  - Production system will be located in the U.S., current utilities costs
  - 500,000 automotive stacks per year with 400 cells each, 80kW
  - 2 shift/day, 8 hrs/shift, 5 days/week, 50 weeks/yr operation of production facility
  - Cost analysis only addresses sealing process

- Our Phase II results are conservative: 29% cost reduction for APC, and 90% cost reduction for U/S sealing
- Greatest benefits of APC may be downstream in stack assembly
- U/S sealing (electrodes to membrane) is a very robust process
- U/S welding (subgasket to electrode) will enjoy similar cost savings

New Data for Task 15.0 (Phase III)

- 96% energy and 93% cycle time reductions (actual) with 50 cm^2 high-temperature MEAs
- 98% energy and 94% cycle time reductions (actual) with 10 cm^2 low-temperature MEAs

Collaborations

- BASF Fuel Cell
  - Supply high temperature membrane and electrodes for all testing
  - Benefit directly from thermal bonding, ultrasonic bonding, and heat treatment results
  - Royalty-free license agreement for use of MEA ultrasonics bonding patent (pending)
- NREL
  - Duplicating performance tests for all thermally and ultrasonically bonded low temperature MEAs
- Progressive Machine & Design (PMD)
  - Working with PMD to continuously improve and ugprade BASF's enhanced pilot line
- Ballard Power Systems
  - Testing of ultrasonically welded MEAs using Ballard low temperature membrane and GDE

Future Work

- Further test 10-cell stack configuration with full diagnostics to determine the effect MEA quality (including purposeful insertion of defective MEAs) on stack performance and steady-state durability
- Determine causes of sub-optimal performance observed with 140 cm^2 thermal & ultrasonic MEAs
- Apply full diagnostics and use thermal characterization to assess quality of 140 cm^2 MEAs subject to different operating conditions
- Perform more diagnostics during the entire MEA build process to gain further insight into sources of manufacturing variation, the importance of membrane/electrode bond integrity prior to heat treatment, and also demonstrate real-time quality control measures
- Update cost analysis and compare discrete manufacturing to roll-to-roll manufacturing approach
- Create design guidelines for ultrasonic tooling and process to bond high- and low-temperature PEM MEAs.

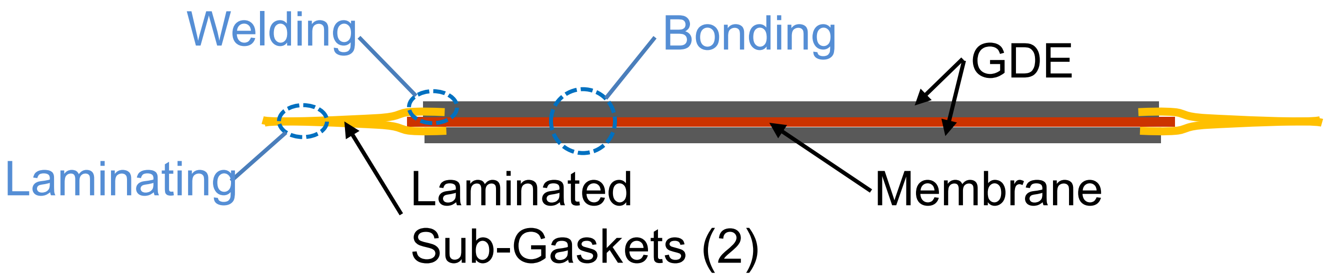
Project Summary

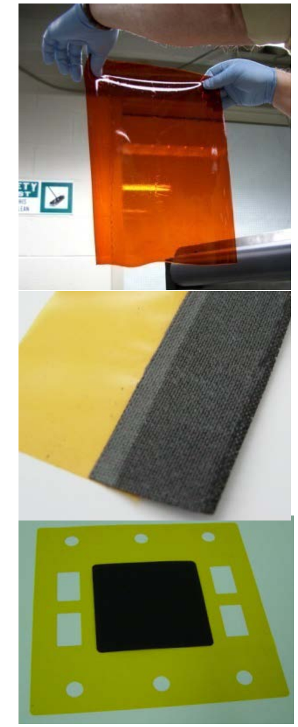
- Ultrasonics and optimized heat treatment result in MEAs manufactured with significant energy, cycle time, and cost savings along with similar performance to thermally bonded MEAs, both high and low temperature types
- Although cycle time reductions of up to 75% are possible with thermal bonding using APC, it still takes 3× longer than thermal bonding and energy consumption is much higher. Hence, R&D focus has shifted (with DOE’s blessing) to ultrasonics only, gaining a better understanding of causes behind manufacturing variation, making improvements to increase process robustness, and fully demonstrating cost, cycle time, and energy saving targets.
- The dominance of heat treatment on high temperature MEA performance may diminish the importance of the bonding method used.
- Stack and large area MEA testing continue to provide critical insight into the potential of ultrasonic bonding in MEA manufacturing.

Technical Backup Slides

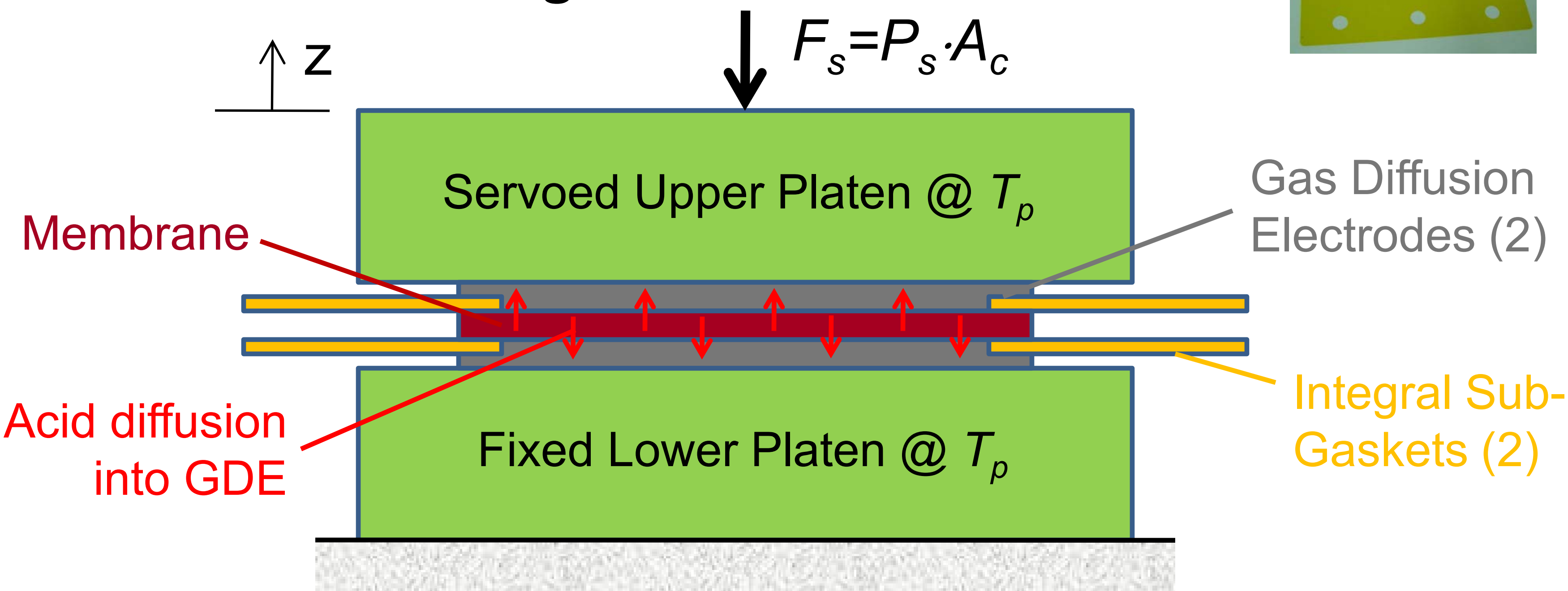
Relevance

- 5-layer MEA Architecture





- Thermal Bonding Procedure

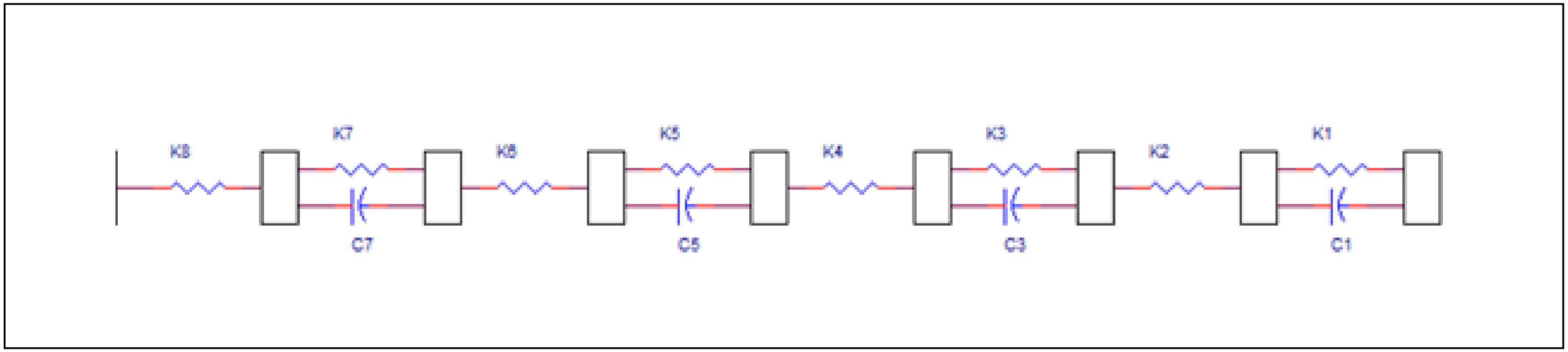


FY2011 Publications/Presentations (published & in review)

- Joe Beck, J., Buelte, S., Walczyk, D. Walczyk, “Comparison of Performance Losses between Ultrasonically and Thermally Bonded MEAs for Low Temperature Fuel Cells,” *Journal of Fuel Cell Science and Technology* (in review).
- S. Buelte, S., Walczyk, D., “Effect of MEA Bonding Technique on Fuel Cell Performance and Platinum Crystallite Size,” *Journal of Fuel Cell Science and Technology* (in review).
- Beck, J., Walczyk, D., Hoffman, C., Buelte, S., “Ultrasonic Bonding of Membrane Electrode Assemblies for Low Temperature PEM Fuel Cells,” *Journal of Fuel Cell Science and Technology* (in review).
- Guglielmo, D., Snelson, T. and Walczyk, D., “Modeling Ultrasonic Sealing of Membrane Electrode Assemblies for High-Temperature PEM Fuel Cells,” *Proceedings of the ASME 9th Fuel Cell Science, Engineering and Technology Conference*, Washington, DC, Aug. 7-10, 2011, Paper # ESFuelCell2011-54427.
- Pyzza, J., W. Sisson, W. and Puffer, R., “Manufacturing Implementation of Ultrasonic Sealing of Membrane electrode assemblies for high temperature PEM fuel cells” *Proceedings of the ASME 9th Fuel Cell Science, Engineering and Technology Conference*, Washington, DC, Aug. 7-10, 2011, Paper # ESFuelCell2011-54441.
- Pyzza, J., “Implementation of Ultrasonic Welders in Automated High Temperature PEM Fuel Cell Membrane Electrode Assembly Manufacturing,” *M.S. Thesis*, Department of Mechanical, Aerospace & Nuclear Engineering, Rensselaer Polytechnic Institute, Troy, NY, 2011.
- Snelson, T., “Ultrasonic Sealing of PEM Fuel Cell Membrane Electrode Assemblies,” Ph.D. Thesis, Department of Mechanical, Aerospace & Nuclear Engineering, Rensselaer Polytechnic Institute, Troy, NY, 2011.
- Puffer, R. and Walczyk, D., “Adaptive Process Controls and Ultrasonics for High Temperature PEM MEA Manufacture,” *Fuel Cell Tech Team Meeting (USCAR)*, Southfield, MI, March 16, 2011.

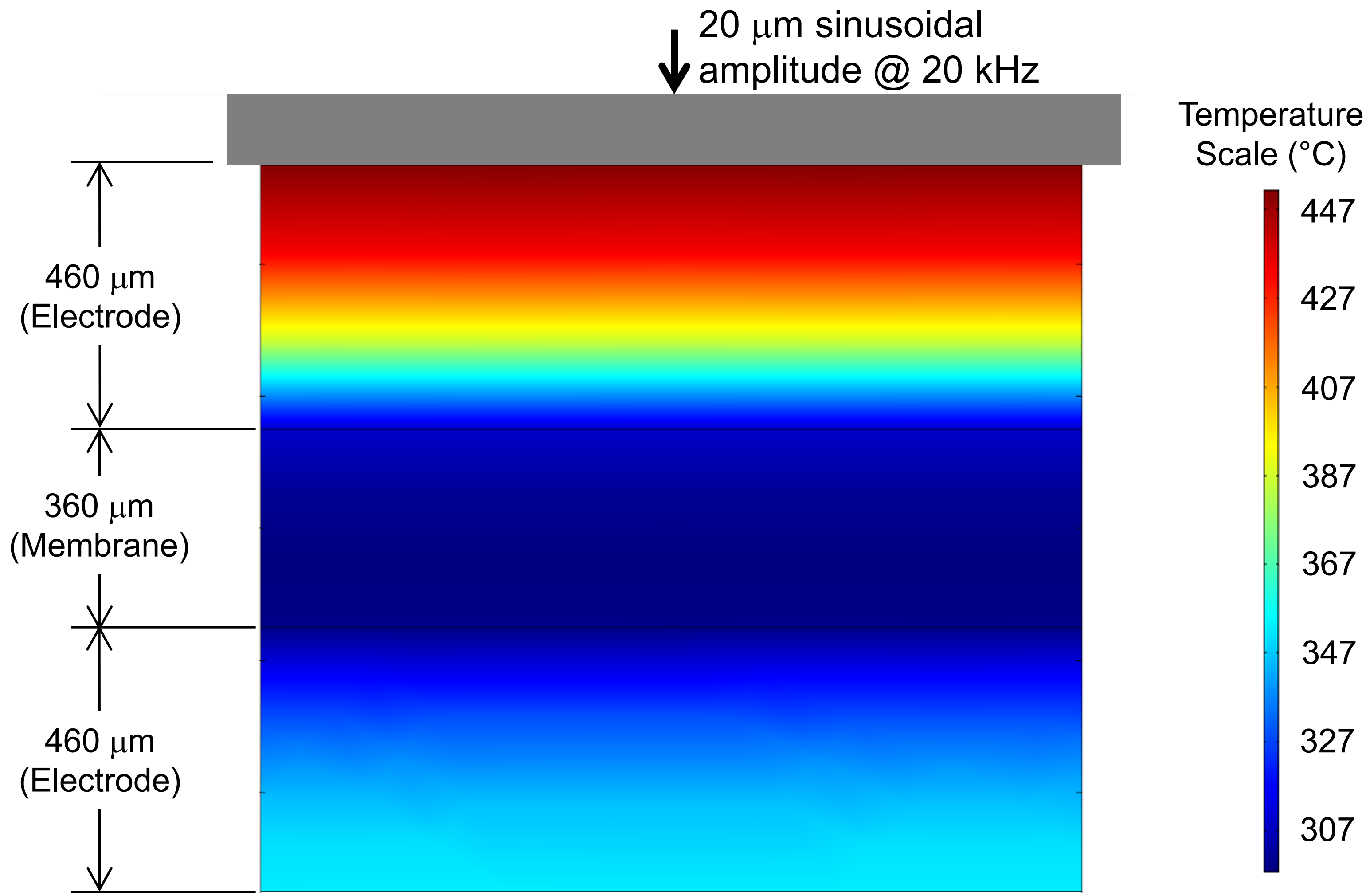
Ultrasonic Analytical Modeling (Continuation of Task 4.0)

- Each physical layer modeled as two mathematical layers
- First two mathematical layers are used to convert the displacement input into a force input
- Given sinusoidal input, a closed form solution for the motion of each degree of freedom can be found
- Differences in velocities across dampers generate heating in MEA
- MEA heating causes rapid temperature rise in each layer, resulting in bonding



Complete System Model

- Comsol FEA model (dynamic thermal) showing through-thickness temperature distribution at 3.5 sec during ultrasonic bonding (with time reference to graph on next slide).



- Membrane/electrode interface temperatures vs. time for simulation (FEA model output) and experimental measurement (via embedded thermocouples)